

OZONE REACTIONS WITH INORGANIC AND ORGANIC COMPOUNDS IN WATER

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Keywords: Metals, micropollutant, natural organic matter, drinking water, wastewater, kinetics.

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Summary

Ozone is a powerful oxidizing agent. Second only to fluorine in its oxidizing power, ozone has many uses including but not limited to water purification, bleaching of

materials such as paper, synthetic fibers, Teflon, waxes, flour, and other products, treatment of wastes in industry, deodorization and sterilization. Previously, chlorine products have been used for these purposes, but recent studies have shown that chlorine products may produce carcinogens such as trihalomethanes and chloramines. Ozone is a safe alternative to chlorine products which performs the same functions without the undesirable side effects; it is not harmful to the environment since it is made from oxygen and decomposes back into oxygen. The most common use of commercially produced ozone is in treatment of water and wastewater such as sewage, wastewaters associated with pulp and paper mills, and waters polluted with pesticides. These toxic wastewaters typically have high concentrations of organochlorine compounds, phenols, amines, pesticides and are highly colored; these pollutants and colored compounds are resistant to conventional methods of treatment. Studies have shown that ozone is a viable alternative to the reducing of concentrations of these above-mentioned pollutants. The oxidative properties of ozone are useful in the removal of soluble iron and manganese, the removal of unwanted colors, tastes, and odors, the decomplexing of bound heavy metals, the destruction of inorganic components such as sulfides, cyanides, and nitrites, and the removal of suspended solids. In these applications the ozone reactions are very rapid and contact time is short. Treatment of drinking water with ozone also can disinfect the water by killing bacteria and inactivating viruses present in the water.

1. Introduction

Water rapidly absorbs both natural and man-made substances generally making the water unsuitable for using prior to some form of treatment. Naturally occurring substances that may need to be reduced or removed in waters include iron, hardness and carbon dioxide. Substances originating from humans are becoming increasingly common in waters, and those requiring treatment include nitrates, pathogens and trace organics.

The objective of water treatment is to produce an adequate and continuous supply of water that is chemically, bacteriologically and aesthetically pleasing. More specifically, water treatment must produce water that is:

- Palatable (i.e. no unpleasant taste);
- Safe (i.e. does not contain pathogens or chemicals harmful to the consumer);
- Clear (i.e. free from suspended solids and turbidity);
- Colorless and odorless (i.e. aesthetic to drink);
- Reasonably soft (i.e. allows consumers to wash clothes, dishes, themselves, without use of excessive quantities of detergents or soap);
- Non-corrosive (i.e. to protect pipe work and prevent leaching of metals from tanks or pipes);

- Low organic content (i.e. high organic content results in unwanted biological growth in pipes and storage tanks that often affects quality).
- Ozone application has increased enormously both in number and diversity since the first full scale application of ozone for the disinfection of drinking water in Nice. Generally, the main areas where ozone is used are:
 - Oxidation of inorganic compounds,
 - Oxidation of organic compounds, including taste, odor, color removal and
 - Disinfection.

2. Oxidation of Inorganic Compounds

The use of ozonation to oxidize metal surfaces in the semiconductor industry is growing, ozonation for the oxidative removal or transformation of inorganic constituents of drinking and waste waters is a rather rare application, because other methods exist for most of the target compounds. However, unwanted inorganic compounds, such as iron, manganese, nitrite, cyanide, and hydrogen sulfide, may be oxidized as a secondary effect of ozonation for other purposes (particle removal, organics oxidation). In these applications the ozone reactions are very rapid and contact time is short (seconds or a few minutes).

2.1. Iron and Manganese Removal

Iron and manganese are two of the most abundant elements found in the earth's crust. Soluble iron and manganese in drinking water are not related to specific health problems but are associated with aesthetic water quality issues, such as discoloration of water, bathroom fixtures, and clothing in clothes washes. Also, growth of iron- and manganese-oxidizing bacteria on water mains can lead to a general deterioration of the quality of the water distributed. For these reasons, standards have been established for maximum concentrations of both soluble species in drinking water. The current European standards observed in EU Directive, 98/83/EC list fixed concentrations at maximum of $50 \mu\text{g L}^{-1}$ for manganese and $200 \mu\text{g L}^{-1}$ for iron. In United States, recommended secondary maximum contaminant levels are $50 \mu\text{g L}^{-1}$ for manganese and $300 \mu\text{g L}^{-1}$ for iron.

The standard oxidation-reduction potential and reaction rate of ozone are such that it can readily oxidize iron and manganese in groundwater and water of low organic content.

The oxidized forms Fe^{3+} and Mn^{4+} are most prevalent, but it is the reduced forms (rhodochrosite [MnCO_3] and siderite [FeCO_3]) that are present in water. The conversion of these carbonates into bicarbonate forms can take place when CO_2 is present, via the following reactions:

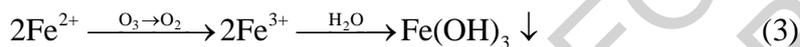


Large concentrations of CO_2 are generally found in ground waters and at the bottom of surface water impoundments where anaerobic conditions are prevalent.

Removal of iron and manganese consists of transforming the soluble matter into insoluble compounds that can be filtered out of the water. Soluble ferrous iron Fe(II) is oxidized to ferric iron Fe(III), which slowly hydrolyzes to form particulate $\text{Fe}(\text{OH})_3$. Manganese oxidation by ozone and subsequent manganese removal is quite complex. Ozone oxidizes soluble manganese [Mn(II)] to form particulate (removable) manganese dioxide [MnO_2 – Mn(IV)].

Iron removal. It is known that in neutral environment the passage from a reduced to an oxidized form is thermodynamically favorable.

The ferrous iron is, therefore, easily oxidized by ozone by the following reactions:

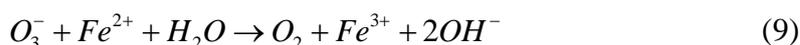


This reaction implies a consumption of $0.43 \text{ mg O}_3 \text{ mg}^{-1}$ of Fe^{2+} . With regard to the process involved, since Fe^{2+} is an O_3 decomposition initiator, it is likely that the reaction proceeds by the transfer of electrons.

The mechanism for this reaction is as follows:

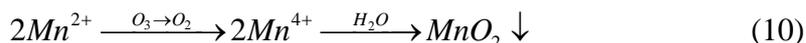


However, reaction (5) is not always dominant, and a direct oxidation of Fe^{2+} with O_3^- is possible. Thus,



Manganese removal. Compared with the different forms of iron the conversion of Mn^{2+} into MnO_2 requires more oxidizing power than the conversion of Fe^{2+} into $\text{Fe}(\text{OH})_3$ because it requires more energy.

The oxidation reaction of manganese by ozone takes the following form:



Due to extremely fast kinetics of iron oxidation, uncomplexed Fe(II) can easily outcompete Mn(II) for ozone. Therefore, in groundwater containing iron, little manganese oxidation occurs at low doses, such that only after the Fe(II) is nearly gone does the oxidation of Mn(II) begin. With groundwater and water of low organic content, the doses of ozone required to completely oxidize iron and manganese are close to the theoretic stoichiometric doses – 0.43 mg O₃ mg⁻¹ Fe and 0.88 mg O₃ mg⁻¹ Mn providing the treated water contains no other ozone-demanding substances, such as nitrites or sulfide.

However, excessive doses will lead to the formation of soluble (nonremovable) permanganate [MnO₄⁻ - Mn(VII)], which gives the water a pinkish color. This soluble form of manganese corresponds to a theoretical stoichiometry of 2.20 mg O₃ L⁻¹ Mn. In the presence of readily oxidizable organics, most, if not all, ozone-produced permanganate can return to the insoluble manganese dioxide, given sufficient time, e.g., 20 to 30 min. Ozone treatment of manganese removal must be implemented carefully to ensure that manganese is captured in the treatment process and that soluble manganese (permanganate) not formed and subsequently discharged from the filters. Reducing permanganate to MnO₂ must occur within the filter.

The oxidation of manganese with ozone is less dependent on pH than for other oxidants. As a result, ozone is more likely to offer kinetic advantages at low pH's than at high pH's. With regard to groundwater, the use of ozone has the additional advantage of reoxygenating the water at the same time.

The presence of organic material in water inhibits the removal of iron and manganese, requiring higher ozone doses and/or longer contact times for effective treatment. Organic matter (for example, as radical scavengers or promoters), may change the main pathway of ozone reactions (direct or indirect), change the specification of the metal (for example, through complexation), or simply compete with the metal for oxidant. It is well-known that humic materials and model organic compounds can complex iron and reduce its susceptibility to oxidation. The degree to which complexed iron is oxidized by ozone is likely to be dependent on the pH and the nature and concentration of organic matter. While low concentrations of humic substances can prevent the oxidation of Fe(II) by oxygen, oxidation by ozone is generally more successful. It was found that high ozone doses caused the oxidation of most of the iron present in water, while at the same time resulting in the formation of some very stable iron-organic complexes that could not be subsequently oxidized. These stable complexes were not formed when the water was simply oxygenated. Humic substances can successfully compete with manganese for ozone, thereby requiring doses far in excess of the stoichiometric values. For this reason, it is best to first remove organics before applying ozone for the purpose of removing manganese. This can be accomplished by raw water coagulation and sedimentation, preferably at an acidic pH (around pH 5) using either aluminum or iron salts (FeCl₃ or FeSO₄Cl).

Laboratory studies on synthetic, reconstituted water and natural water high in iron,

manganese, fulvic, and humic acids have shown that for a fixed alkalinity (150 mg L^{-1} of CaCO_3) and at a constant ozone/DOC application rate, the unoxidized manganese residual after treatment increases as the organic concentration increases. For the water under study (pH=8.5, manganese concentration in the region of $250 \text{ } \mu\text{g L}^{-1}$), a dose of $0.3 \text{ mg O}_3 \text{ mg}^{-1} \text{ C}$ resulted in manganese residual, after filtration, of less than $60 \text{ } \mu\text{L}^{-1}$; an ozonation dose of $0.5 \text{ mg O}_3 \text{ mg}^{-1} \text{ C}$ resulted in a filtered-water manganese residual of under $30 \text{ } \mu\text{g L}^{-1}$. On the other hand, higher levels of ozone ultimately led to the formation of permanganate, which persisted through filtration. In addition to effective manganese removal, intermediate recarbonation and ozonation can lead to a reduction in the UV absorbance of the filtered water and in the concentration of trihalomethane (THM) precursors.

Another study using synthetic water (pH 6.3, $1 \text{ mg L}^{-1} \text{ Mn(II)}$, $2\text{-}5 \text{ mg L}^{-1}$ total organic carbon (TOC), $50\text{-}200 \text{ CaCO}_3 \text{ L}^{-1}$) showed that 75 percent manganese removal was achieved after application of an ozone dose of $0.2\text{-}0.7 \text{ mg O}_3 \text{ mg}^{-1} \text{ C}$ in excess of that required for manganese oxidation alone (according to the theoretical stoichiometry). The precise excess ozone dose depended on the bicarbonate concentration: the presence of high levels of bicarbonate can modify consumption of oxidant such that less ozone is required.

Once the manganese is oxidized to Mn(III) or Mn(IV), it can be removed by flocculation and sedimentation, rapid sand filtration, or multi-media filtration. Filtration through “aged” sand is especially efficient as it also permits the removal of small amounts of reduced manganese. With time, the sand grains become coated with oxides of manganese and iron, and exhibit the “greensand” effect. This is a catalytic phenomenon that includes adsorption of Mn(II) on the oxide surface and subsequent oxidation. For this latter process to occur over long periods of time, the sand surface must be periodically exposed to a chemical oxidant such as chlorine or permanganate. The oxidants undergo a redox reaction at the oxide surface, thereby renewing its oxidative power. As a result, small amounts of permanganate can be removed through filtration; however, excessive amounts will result in breakthrough.

2.2. Halogens Removal

The standard oxidation-reduction potential (E^0) values applicable to the combination O_3/O_2 and the various halogen/halide couples are as follows:

| | E^0, V |
|---------------------------|----------|
| O_3/O_2 | 2.07 |
| HClO/Cl^- | 1.49 |
| HBrO/Br^- | 1.33 |
| HIO/I^- | 0.99 |

Therefore, it is thermodynamically possible for ozone to oxidize chloride, bromide, and iodide. In fact, when bromide or iodide ions are present in waters being ozonated, free bromine (Br_2) and/or hypobromous acid (HOBr), hypobromite ion (BrO^-), bromate ion (BrO_3^-), free iodine (I_2), and/or hypoiodous acid (HOI), hypoiodite ion (IO^-), and iodate ion (IO_3^-) are some of the halogen-containing oxidants that can be produced. The rate of reaction is very high in the case of the iodides. It is slower for bromides and practically

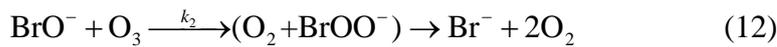
zero for chlorides.

Bromide ion is oxidized into hypobromite according to the following reaction:



where $k_1 = 160 \text{ M}^{-1}\text{s}^{-1}$

The hypobromite formed can be partially oxidized into bromate ion, while a part of the bromide is regenerated through the following reactions:



where $k_2 = 330 \text{ M}^{-1}\text{s}^{-1}$, $k_3 = 100 \text{ M}^{-1}\text{s}^{-1}$

The overall reaction is as follows:



It is interesting to note that for lower pH values, less bromate is formed.

2.3. Oxidation of Ammonia

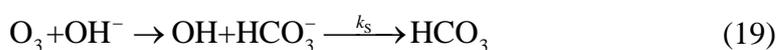
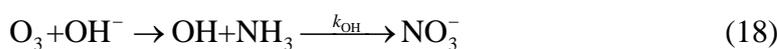
Ammonia can be oxidized by the following reaction:



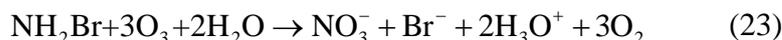
with

$$-d \frac{[\text{NH}_3]}{dt} = k[\text{NH}_3][\text{O}_3] \quad (16)$$

The ammonia oxidation is slow, especially at pH levels below the pK_a (about 9.3). The oxidation of ammonia most likely results from the superposition of the direct reaction produced by molecular ozone and the indirect reaction of the OH radicals formed by the decomposition of ozone (17-19). The share of indirect reaction is inversely proportional to the pH level.



The existence of bromide in water may catalyze the degradation of ammonia. The hypobromous acid formed by the oxidation of bromide quickly leads to the formation of monobromamine, which in turn is oxidized by ozone resulting in the release of bromide and nitrate. This is shown in the following reactions:



The overall reaction is as follows:



As bromide is regenerated by the system, it, in effect, plays the part of a catalyst. Moreover, the monobromamine oxidation rate is somewhat faster than that of ammonia and, above all, is independent of the pH. This allows indirect oxidation of the ammonia in a neutral pH environment to occur at a faster rate than would occur during direct ozonation.

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Biographical Sketch

Elina Portjanskaja was born in Tallinn, Estonia on March 27, 1981. Elina Portjanskaja received her Master of Chemical and Environmental Protection Technology from Tallinn University of Technology (TUT) in Tallinn, Estonia, 2005, and Master of Science in Chemical Technology from Lappeenranta University of Technology (LUT) in Lappeenranta, Finland, 2005. At the moment Elina Portjanskaja is continuing her doctoral studying at TUT with prospective defense in 2009.

Her work experience includes: Researcher (2000-present) TUT in Tallinn, Estonia, Researcher (2004, 6 months) LUT, Researcher (2003, 5 months) sponsored by Centre of International Mobility (CIMO), the International Association for the Exchange of Students for Technical Experience (IAESTE) and EKOKEM Ltd. Articles: Portjanskaja E., Preis S. and Kallas J. (2006). Aqueous photocatalytic oxidation of lignin and humic substances with supported TiO₂. *International Journal of Photoenergy*. **2006**. ISSN: 1110-662X; Klauson D., Portjanskaja E., Kachina A., Krichevskaya M., Preis S. and Kallas J. (2005). The influence of ferrous/ferric ions on the efficiency of photocatalytic oxidation of pollutants in groundwater. *Environmental Technology*. **26**, 653-662; Portjanskaja E., Krichevskaya M., Preis S. and Kallas J. (2004). Photocatalytic oxidation of humic substances with TiO₂-coated glass micro-spheres. *Environmental Chemistry Letters*. **2**(3), 123-127.

Current and previous research interests: Photocatalytic Oxidation of Waters Containing Humic Substances and Lignin.